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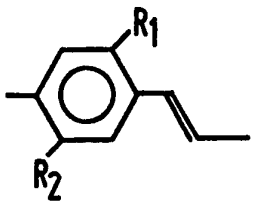
(54) Title: LIGHT-EMITTING DIODE COMPRISING AN ACTIVE LAYER OF 2,5-SUBSTITUTED POLY(P-PHENYLENE VINYLENE)

(57) Abstract

A description is given of a LED comprising an active layer of novel, conjugated 2,5-alkyl-substituted poly(p-phenylene vinylene) compounds having a repeating unit (I). Said LED emits green light. In these polymers, R_1 represents a C_{10}-C_{12} alkyl group and R_2 represents a C_1-C_4 alkyl group. These polymers can readily be dissolved in organic solvents, so that an active layer can be manufactured in a simple manner by means of spin coating.



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Light-emitting diode comprising an active layer of 2,5-substituted poly(p-phenylene vinylene).

The invention relates to a light-emitting diode comprising an active layer which contains conjugated 2,5-substituted poly(p-phenylene vinylene) (PPV) and which layer is situated between two electrode layers, at least one of which is translucent. The invention also relates to novel, soluble, conjugated 2,5-substituted poly(p-phenylene vinylene) compounds. The invention further relates to a method of manufacturing an electroluminescent (EL) device, in particular a light-emitting diode (LED), in which use is made of such a conjugated polymer.

Solid-state LEDs have found widespread application, for example, in displays and indicator lamps. For the active or emissive layer in EL structures, use is generally made of traditional III-V semiconductor compounds, such as doped GaAs and GaP. The action is based on recombinations of electron-hole pairs which are injected into the semiconductor material from electrodes situated on either side of the active layer. By virtue of these recombinations, energy is released in the form of (visible) light; this phenomenon is commonly referred to as electroluminescence. The wavelength and hence the colour of the emitted light is determined by the band gap of the semiconductor material.

Using the known technologies in combination with the above-mentioned inorganic semiconductor materials, it is very difficult to manufacture large-area displays having dimensions of, for example, several centimetres. In addition, the available colours of the emitted light are limited to the long wavelength end of the visible spectrum.

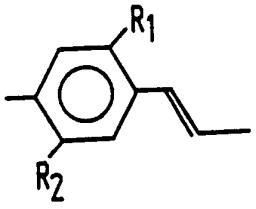
The use of semiconductive organic polymers expands the number of materials which can be used in EL devices. Semiconductive organic polymers have a conjugated polymeric chain. The band gap, the electron affinity and the ionization potential can be adjusted by choosing the proper conjugated polymeric chains and suitable side chains. Unlike electroconductive polymers, these conjugated polymers are undoped. In addition, such polymers enable the use of flexible substrates. An active layer of such a polymeric material can be manufactured by means of a CVD process, using a suitable monomer as the starting material, or by spin coating a solution of a soluble, non-conjugated polymeric precursor which is converted into conjugated polymer by a thermal post-treatment.

The international Patent Application WO 92/16023 discloses a soluble, conjugated 2,5-substituted poly(p-phenylene vinylene), namely poly(2-methoxy, 5-(2'-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV). This conjugated PPV which is substituted with two alkoxy substituents can be dissolved in various organic solvents and provided on a substrate carrying an electrode material by spin coating of a solution. After the solvent has evaporated, without a further thermal post-treatment, an active layer having electroluminescent properties is obtained. A second electrode layer is provided on the active layer. One of the electrode layers is translucent. The structure obtained is that of an LED, which emits light at room temperature in the yellow-orange range of the spectrum.

In practice, however, there is a need for LEDs emitting colours other than yellow-orange at room temperature. In said Patent Application, PPV compounds other than those substituted with two alkoxy groups are not stated nor is it stated in said document which conjugated polymer can be used to manufacture an LED which emits green light.

It is an object of the invention to provide, *inter alia*, an LED whose active layer comprises conjugated 2,5-substituted PPV and emits light in the green range of the spectrum. The invention further aims at providing a simple method of manufacturing such an LED, in which method the active layer is manufactured from a solution of the conjugated PPV, in particular by spin coating, and does not require a thermal post-treatment. A further object of the invention is to provide novel, conjugated 2,5-substituted PPV compounds which are soluble in an organic solvent and which exhibit an electroluminescent effect, so that they can suitably be used in an active layer of an EL device, in particular a LED.

These objects are achieved by a LED as described in the opening paragraph, which is characterized according to the invention in that the poly(p-phenylene vinylene) comprises a repeating unit of the formula



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wherein R_1 represents an C_{10}-C_{12} alkyl group and R_2 represents a C_1-C_4 alkyl group.

Unlike the conjugated MEH-PPV disclosed in the above-mentioned Patent Application WO 92/16023, such a conjugated polymer does not comprise alkoxy groups, but alkyl groups. It has been found that a LED whose active layer comprises a conjugated PPV having a repeating unit in accordance with formula (I) emits green light. In addition, a conjugated polymer having repeating unit (I) can readily be dissolved, namely 1 to 3 wt.%, in many organic solvents, such as toluene, xylene, tetrahydrofuran and mixtures of said solvents, so that the active layer of the LED can be manufactured by, for example, spin coating. The alkyl substituents R_1 and R_2 in formula (I) may be unbranched or branched.

Suitable alkyl substituents R_1 are the 3,7-dimethyl octyl group (C_{10}) the 4,6,6-trimethyl heptyl group (C_{10}), the n-undecyl group (C_{11}) and the n-dodecyl group (C_{12}).

Suitable alkyl substituents R_2 are the methyl group (C_1), the ethyl group (C_2), the propyl group (C_3) and the n-butyl group (C_4).

The use of just these alkyl substituents R_1 and R_2 is based on the observation that alkyl substituents of different size have a positive effect on the solubility of the conjugated PPV. If, per aromatic ring, two equal alkyl substituents are used, for example $R_1 = R_2 = C_5$-alkyl, the conjugated PPV is practically insoluble in organic solvents. If, per aromatic ring, two equal alkyl substituents R_1 and R_2 are used, which are longer than a C_5 alkyl group, the solubility increases only slowly. The combination of a short alkyl substituent R_2 and a long alkyl substituent R_1 per aromatic ring causes the conjugated PPV to be readily soluble in organic solvents, and the emission of green light is preserved when said PPV is used in an active layer of an LED. It has been found that the use of alkyl substituents R_1, which are longer than C_{12} alkyl, does not result in a noticeable further increase of the solubility; besides, the quantity of active material per gram of conjugated PPV decreases due to the presence of longer alkyl substituents. Preferably, branched alkyl substituents R_1 are used, because they can be readily dissolved.

It is noted that in European Patent Application EP-A-443861, conjugated 2,5-substituted PPV compounds are mentioned which are substituted with two equal C_1 to C_{22}

alkyl substituents per aromatic ring, for example two methyl, ethyl, heptyl, octyl or lauryl substituents per aromatic ring. It has been found that these compounds exhibit a very poor solubility in organic solvents, so that a spin coated layer of such a polymer becomes inhomogeneous or too thin. The exemplary embodiments in said Patent Applications only give examples of conjugated PPV which is 2,5-substituted with two heptyloxy groups (alkoxy groups comprising 7 C-atoms). It is stated that a LED comprising an active layer of such a polymer emits light in the yellow-orange range of the spectrum. In said European Patent Application there is no indication of the use of two unequal alkyl substituents R_1 and R_2 which have the above-mentioned meaning and by means of which a LED emitting green light can be manufactured.

Dependent upon the method of preparing the conjugated polymer, which method will be specified hereinbelow, the polymer may comprise 5 to 10% of non-conjugated units. It has been found that such non-conjugated units increase the electroluminescent efficiency, which is defined by the number of photons per electron injected into the active layer.

The degree of polymerization n of the conjugated polymer ranges between 10 and 100,000.

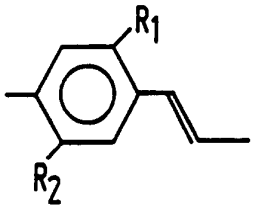
The active layer of the conjugated polymer having repeating unit (I) generally has a layer thickness in the range between 50 and 200 nm, in particular between 100 and 200 nm.

The LED structure is provided on a substrate which consists, for example, of glass, quartz glass, ceramic material or synthetic resin. Preferably, a translucent or transparent substrate is used, for example a transparent, flexible foil of synthetic resin. Suitable transparent synthetic resins are, for example, polyimide, polyethylene terephtalate and polytetrafluoroethylene.

The active layer is situated between two electrode layers of electroconductive materials. At least one of said electrode layers must be transparent or transmit the light emitting from the active layer. One of the electrode layers serves as the electrode for the injection of holes into the active layer. The material of this electrode layer has a high work function and is constituted, for example, by a thin layer of gold or silver, or preferably a layer of indium oxide or indium-tin oxide (ITO). Such layers are transparent to the light emitting from the active layer. Particularly ITO is suitable owing to the fact that it has a good electroconductivity and a high degree of transparency. The other electrode layer serves as the electrode for the injection of electrons into the active layer. The material of this

layer has a low work function and consists of a layer of, for example, indium, calcium, barium or magnesium. In particular when use is made of the reactive barium it is efficacious to cover said second electroconductive layer with a protective layer, for example, of epoxy or an inert metal.

The invention also relates to novel 2,5-substituted poly(p-phenylene vinylene) compounds which can suitably be used in EL devices, the repeating unit of said compounds can be given by the formula



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wherein R_1 represents a C_{10}-C_{12} alkyl group and R_2 represents a C_1-C_4 alkyl group. Examples of suitable alkyl substituents R_1 and R_2 are mentioned hereinabove.

Suitable polymers in accordance with the invention are:

poly[2-methyl-5-(n-dodecyl)-p-phenylene vinylene],

poly[2-methyl-5-(3,7-dimethyl octyl)-p-phenylene vinylene],

poly[2-methyl-5-(4,6,6-trimethyl heptyl)-p-phenylene vinylene].

Said conjugated polymers are readily soluble in organic solvents and emit green light if they are used as an active layer in a LED. The polymers in accordance with the invention may also contain different repeating units (I) by using a mixture of the corresponding monomers in the polymerization reaction which will be elucidated hereinbelow.

The object of providing a method of manufacturing a LED is achieved in accordance with the invention by a method which is characterized by the following steps:

a. providing a substrate with a first, electroconductive electrode layer,

b. providing said first layer with a solution of a conjugated 2,5-substituted poly(p-phenylene vinylene) having a repeating unit in accordance with formula (I), wherein R_1 and R_2 have the above-mentioned meaning, in a solvent, whereafter the solvent is evaporated, thereby forming the active layer,

c. providing the active layer with a second, electroconductive electrode layer.

For the substrate use can be made of the above-mentioned inorganic substrates, however, preferably use is made of transparent, flexible polymeric substrates, such as substrates of polyimide, polytetrafluoroethylene or polyethylene terephtalate.

The substrate is provided with a, preferably transparent, first electroconductive layer which serves as the electrode layer for the injection of holes into the active layer of conjugated PPV to be provided on said electroconductive layer. For the material of this electrode layer use can be made of the above-mentioned materials, such as a thin layer of gold or silver or a layer of indium oxide or indium-tin oxide (ITO). Particularly ITO is very suitable due to its good electroconductivity and high transparency. This first layer can be provided on the substrate by methods which are known *per se*, such as vacuum evaporation, sputtering or a CVD process.

Subsequently, the active layer of conjugated 2,5-substituted PPV is provided on this first, electroconductive layer. This active layer is provided on the substrate from a solution of the conjugated PPV in a solvent. To provide this layer use can be made of all methods which are known *per se*, but preferably the layer is provided by spin coating. The layer thickness of the active layer generally ranges between 50 and 200 nm and depends, *inter alia*, on the concentration of the polymer in the solvent and on the rotational speed during spin coating. The layer can be provided at room temperature, and apart from the evaporation of the solvent no further thermal post-treatment is required. By virtue thereof, many synthetic resin substrates which are not resistant to high temperatures can be used.

The active layer is provided with a second, electroconductive layer which serves as the electrode layer for the injection of electrons into the active layer. For the material of this electrode layer use can be made of the above-mentioned materials, such as indium, calcium, barium or magnesium. This second layer can alternatively be provided by the above-mentioned methods. In particular when use is made of reactive barium, it is efficacious to cover this second electrode layer with a protective layer, for example, of epoxy or an inert metal.

The invention will be explained in greater detail by means of exemplary embodiments and drawings, in which

Fig. 1 shows the reaction scheme of the preparation of 1,4-dialkylbenzenes,

Fig. 2 shows the reaction scheme of the preparation of 1-(3,7-dimethyl

octyl)-4-methylbenzene,

Fig. 3 shows the reaction scheme of the preparation of 1-(4,6,6-trimethyl heptyl)-4-methylbenzene,

Fig. 4 shows the reaction scheme of the preparation of bischloromethyl compounds on the basis of 1,4-dialkylbenzenes,

Fig. 5 shows the reaction scheme of the polymerization of bischloromethyl compounds into conjugated 2,5-alkyl-substituted PPV,

Fig. 6 shows the formulas I, II and III of repeating units of conjugated 2,5-alkyl-substituted PPV in accordance with the invention,

Fig. 7 is a diagrammatic cross-sectional view of an EL device, in particular a LED, comprising an active layer of conjugated 2,5-alkyl-substituted PPV in accordance with the invention, and

Fig. 8 shows an I-V and L-V characteristic of a LED manufactured by means of conjugated 2,5-alkyl-substituted PPV in accordance with the invention.

Exemplary embodiment 1.

The conjugated 2,5-alkyl-substituted PPV compounds are prepared by polymerization of bischloromethyl-dialkylbenzene compounds. Hereinbelow, a description will be given of the preparation of, in succession, 1,4-dialkylbenzene compounds, the corresponding bischloromethyl compounds and the polymerization thereof to form the desired conjugated PPV compounds.

Preparation of 1,4-dialkylbenzenes.

a. 1-dodecyl-4-methylbenzene; 1-dodecyl-4-ethylbenzene and 1-dodecyl-4-butylbenzene (formula a in Fig. 1).

Fig. 1 shows the reaction scheme of the preparation of 1,4-dialkylbenzenes, wherein R_2 represents, in this example, a CH_3, C_2H_5 or n-C_4H_9 group.

These alkylbenzenes are prepared by means of the following general procedure. A quantity of 110 ml lauroylchloride (0.48 mol) is added, while cooling, to a mixture of $AlCl_3$ (66 g, 0.5 mol) and 250 ml dichloromethane within 30 minutes. The mixture is stirred at room temperature until all the $AlCl_3$ has reacted. The solution is cooled

by means of ice, whereafter ethylbenzene (74 g, 0.7 mol) is added within 1 hour. The mixture is stirred at room temperature for 18 hours and subsequently poured on ice. The layers are separated after which the aqueous layer is extracted with dichloromethane. The combined organic layers are washed with water, dried and evaporated. The residue is purified by means of bulb-to-bulb distillation, thereby forming a solid, main fraction of 125 g. This solid is hydrogenized with Pd on carbon in 600 ml ethyl acetate until the hydrogen absorption stops and NMR analysis shows that the conversion is complete. After filtration, evaporation and bulb-to-bulb distillation, 114 g colourless oil (0.416 mol, 87%) is obtained which is used in the chloromethylation reaction which will be described hereinbelow.

The preparation of 1-dodecyl-4-butylbenzene takes place in a similar manner. In the case of 1-dodecyl-4-methylbenzene, the intermediate compound dodecanoyl toluene is purified by bulb-to-bulb distillation, followed by recrystallization from methanol.

b. Preparation of 1-(3,7-dimethyl octyl)-4-methylbenzene (formula b in Fig. 2).

The reaction scheme is shown in Fig. 2.

1-chlorotoluene (155 g, 1.225 mol) is added for 1 hour to a stirred mixture of sodium wire (53,6 g, 2.33 mol) and 650 ml hexane, the temperature being maintained below 30°C by means of cold water. The mixture is subsequently stirred at room temperature for 18 hours, whereafter 221 g (1 mol) 1-bromo-3,7-dimethyl octane (obtained by reacting the, commercially available, corresponding dimethyl octyl alcohol with 47% HBr in water) is added in 15 minutes, the temperature being maintained below 28°C by means of ice. Subsequently, the mixture is placed on a hot-water bath, which is removed when the reaction temperature has reached 45°C. When the temperature of the exothermal reaction has reached 65°C, the mixture is placed on a cold-water bath. After completion of the exothermal reaction, the mixture is refluxed for 1 hour, whereafter remnants of sodium are destroyed by means of 100 ml ethanol. Subsequently, water is added and the layers are separated. The organic layer is washed with 2 times 500 ml water, dried, evaporated and purified by bulb-to-bulb distillation, thereby forming a main fraction of 149.2 g (0.60 mol, 60%), which fraction is used in the chloromethylation reaction.

c. Preparation of 1-(4,6,6-trimethyl heptyl)-4-methylbenzene (formula c in Fig. 3).

The reaction scheme is shown in Fig. 3. A quantity of 186 ml tetramethylethylene diamine (TMEDA) is added to 492 ml of 2.5 mol/l n-butyllithium in

hexane (1.23 mol), thereby causing an exothermic effect. p-xylene (410 ml, 3.35 mol) is added to the cooled solution, causing an exothermic reaction. The mixture is refluxed for 1 hour and subsequently cooled with ice water. A quantity of 215 g (1.32 mol) 1-chloro-3,5,5-trimethylhexane (prepared by the reaction of the corresponding hexylalcohol with thionylchloride) is added to the mixture for 1.5 hours, the temperature being maintained below 40°C. Subsequently, the mixture is refluxed for 4 hours and then stirred at room temperature for 18 hours. Subsequently, water is added and the layers are separated. The organic layer is washed with water and the aqueous layers are extracted by means of hexane. The organic layers are dried, evaporated and distilled at a temperature of 125°C and a pressure of 0.7 mbar. The yield is 130 g (0.56 mol, 42%).

Preparation of bischloromethyl compounds.

The reaction scheme is shown in Fig. 4. In the following examples, R_2 is a CH_3 group, a C_2H_5 group or an n-C_4H_9 group; R_1 is a dodecyl group, a 3,7-dimethyl octyl group or a 4,6,6-trimethyl heptyl group.

d. 1,4-bischloromethyl-2-dodecyl-5-methylbenzene (formula d in Fig. 4, wherein R_1 = dodecyl and R_2 = methyl).

A quantity of 100 ml sulphuric acid is added to a mixture of 550 ml acetic acid, 116 g 4-dodecyltoluene (formula a in Fig. 1, wherein R_2 = methyl) and 45 g paraformaldehyde (1.5 mol). The stirred mixture is heated to 80°C, while HCl is bubbled through said mixture for 32 hours. The cooled reaction mixture is extracted with three times 500 ml pentane. The combined pentane layers are washed twice with water, whereafter they are dried and filtered over a small aluminium-oxide column. The filtrate is evaporated and the residue is recrystallized from hexane. This yields 23 g of pure product (64 mmol, 14%).

e. 1,4-bischloromethyl-2-dodecyl-5-ethylbenzene (formula d in Fig. 4, wherein R_1 = dodecyl and R_2 = ethyl).

The preparation of this compound is analogous to that of the previous compound. The raw product obtained after filtration over aluminium oxide is purified by bulb-to-bulb distillation (170°C, 0.2 mbar) and the distillate is recrystallized from hexane. A quantity of 14.5 g of pure product (39 mmol, 11%) is obtained from 95 g dodecylethylbenzene (formula a in Fig. 1, wherein R_2 = ethyl).

f. 1,4-bischloromethyl-2-dodecyl-5-butylbenzene (formula d in Fig. 4, wherein R_1 = dodecyl and R_2 = n-butyl).

The preparation of this compound is analogous to that of the previous compound. The raw product obtained after filtration over aluminium oxide is purified by bulb-to-bulb distillation (170°C, 0.2 mbar) and the distillate is recrystallized from hexane.

A quantity of 23 g of pure product (57.6 mmol, 17%) is obtained from 100 g dodecylbutylbenzene.

g. 1,4-bischloromethyl-2-(3,7-dimethyl octyl)-5-methylbenzene (formula d in Fig. 4, wherein R_1 = 3,7-dimethyl octyl and R_2 = methyl).

The preparation of this compound is analogous to that of the previous compound. The raw product obtained after filtration over aluminium oxide is purified by bulb-to-bulb distillation (170°C, 0.2 mbar) and the distillate is recrystallized from hexane. A quantity of 55 g of pure product (0.167 mo, 29%) is obtained from 135.8 g 1-(3,7-dimethyl octyl)-4-methylbenzene (formula b in Fig. 2).

h. 1,4-bischloromethyl-2-(4,6,6-trimethyl heptyl)-5-methylbenzene (formula d in Fig. 4, wherein R_1 = 4,6,6-trimethyl heptyl and R_2 = methyl).

A quantity of 110 ml concentrated sulphuric acid is added to a stirred mixture of 130 g (0.56 mol) 1-(4,6,6-trimethyl heptyl)-4-methylbenzene (formula c in Fig. 3), 300 ml acetic acid, 48 g paraformaldehyde (1.6 mol) and 100 g NaCl (1.71 mol). The mixture is stirred at room temperature for 18 hours, whereafter 30 g NaCl and 30 ml concentrated sulphuric acid are again added. The mixture is subsequently heated to 65°C for 24 hours, whereafter 50 ml concentrated sulphuric acid is added. The mixture is then heated to 60°C for 24 hours. After cooling, 60 g NaCl and 100 ml concentrated hydrochloric acid are added, whereafter the mixture is heated to 75°C for 24 hours. The hot mixture is poured in water, pentane is added and the mixture is filtered over Celite. The layers are separated and the aqueous layer is extracted twice with pentane. The combined pentane layers are washed with water, dried and evaporated. The residue is distilled under a vacuum to separate the monochloromethyl compound (168-172°C, 0.5 mbar) and a mixture of the monochloromethyl and bischloromethyl compound at 172-182°C. The residue is distilled in a bulb tube, thereby forming 97.5 g of the desired compound (0.296 mol, 53%).

Synthesis of conjugated 2,5-substituted poly(p-phenylene vinylene).

Fig. 5 shows the reaction scheme of the synthesis of conjugated 2,5-alkyl-substituted PPV f, using bischloromethyl compounds d as the starting material. R_1 and R_2 have the above-mentioned meaning. In the following exemplary embodiment, a description is given of the preparation of poly[2-methyl-5-(3,7-dimethyl octyl)-p-phenylene vinylene] in accordance with formula f, wherein R_1 = 3,7-dimethyl octyl and R_2 = methyl. The preparation of the other conjugated polymers takes place in a similar manner.

In nitrogen, 2 g of 2-methyl-5-(3,7-dimethyl octyl)-1,4-bis(chloromethyl) benzene d is dissolved in 400 ml dried tetrahydrofuran (THF) in a three-neck bottle. The solution is cooled to -50°C and a solution of 1.1 equivalent potassium-t-butylate (t-BuOK) in 100 ml dried THF is slowly added. When all the t-BuOK is added, the temperature of the mixture is slowly increased to 0°C. Of said mixture, a quantity of 50% by volume of the THF is removed by distillation and the polymer e obtained is precipitated in methanol. Said precipitate is filtered, washed in methanol and dried at room temperature under a vacuum (4.10^{-3} mbar).

The polymer obtained is the non-conjugated chloro-precursor e. To obtain the conjugated polymer, a quantity of 2 g of said precursor e is dissolved in 400 ml cyclohexanone, thereby forming a 0.5 wt.% solution. Dependent upon the desired number of non-conjugated units m, methanol is added to the solution. The addition of for example 10 ml methanol to 400 ml cyclohexanone renders a conjugated polymer f comprising, approximately, a fraction m = 10% of non-conjugated units. If no methanol is added, a fully conjugated polymer f in which m = 0% is obtained. In these formulas, the degree of polymerization n = 10-100,000. A small fraction (m = 5-10%) of non-conjugated units results in an increase of the efficiency of the active layer.

The solution is subsequently heated to 130°C in nitrogen for 12 hours. The solution is then cooled and the polymer f is precipitated in methanol, filtered, washed with methanol and dried under a vacuum. The conjugated polymer f thus obtained, having repeating unit (I) of Fig. 6, can readily be dissolved (up to 3 wt.%) in toluene, THF and xylene.

Exemplary embodiment 2.

In Fig. 7, reference numeral 1 denotes a schematic representation of a cross-sectional view of a polymeric LED structure. A transparent indium-tin oxide layer (ITO) 5 having a surface resistance below 20 Ω/square is sputtered on to a glass substrate 3. This layer 5 serves as the electrode layer for injecting holes in the active layer 7 which is to

be subsequently provided and which consists of conjugated PPV having a repeating unit (I) (Fig. 6). This active layer has a thickness of 150 nm and is manufactured by spin coating an 1-3 wt.% solution of a conjugated 2,5-alkyl-substituted PPV in accordance with the invention. For the solvent use can be made of toluene, xylene, THF or mixtures of said solvents. A calcium layer 9 is provided on the active layer 7 by evaporation at a pressure below 2.10^{-4} Pa. The calcium layer 9 has a layer thickness of 250 nm and serves as the electrode for injecting electrons into the active layer 7. The size of the polymeric LED is 1 cm^2.

The two electrode layers 5 and 9 are connected to a direct-current source, the calcium electrode 9 being connected to earth. The polymeric film 7 of conjugated PPV in accordance with the invention always emits homogeneous, green light which is clearly visible under daylight circumstances. In the completely conjugated state (fraction m = 0%), an efficiency of 0.2% is attained, *i.e.* two photons are generated per 1000 electrons injected into the active layer.

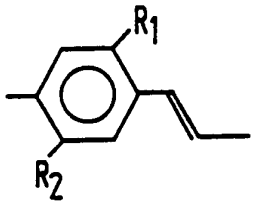
Fig. 8 shows the characteristic of the LED obtained, the current I, in ampere, being plotted as a function of the applied voltage V, in volts, between the electrodes. In addition, the quantity of light L (electroluminescence) is shown in arbitrary units (a.u.) as a function of the voltage V. In the example, poly[2-methyl-5-(3,7-dimethyl octyl)-p-phenylene vinylene] (repeating unit formula II of Fig. 6) is used as the active layer. The LED emits green light in the range between 480 and 650 nm, with maximum emission around 530 nm.

A LED having poly[2-methyl-5-(n-dodecyl)-p-phenylene vinylene] (repeating unit formula III of Fig. 6) as the active layer is manufactured in the same manner. Said LED emits green light in the range between 480 and 650 nm, with maximum emission around 560 nm.

The method in accordance with the invention enables polymeric LEDs having a large surface area to be manufactured in a simple manner by means of spin coating, the active layer of said LEDs being constituted by a conjugated 2,5-alkyl-substituted PPV. The LEDs obtained emit green light. The method can very suitably be used for the manufacture of LEDs on large, flexible substrate surfaces.

Claims:

1. A light-emitting diode comprising an active layer which contains conjugated 2,5-substituted poly(p-phenylene vinylene) and which layer is situated between two electrode layers, at least one of which is translucent, characterized in that the poly(p-phenylene vinylene) comprises a repeating unit of the formula



(I)

wherein R_1 represents a C_{10}-C_{12} alkyl group and R_2 represents a C_1-C_4 alkyl group.

2. A light-emitting diode as claimed in Claim 1, characterized in that R_1 represents a 3,7-dimethyl octyl group and R_2 represents a methyl group.

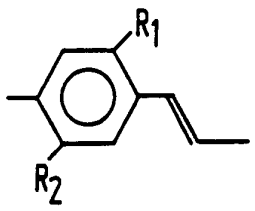
3. A light-emitting diode as claimed in Claim 1, characterized in that R_1 represents an n-dodecyl group and R_2 represents a methyl group.

4. A light-emitting diode as claimed in Claim 1, characterized in that R_1 represents an n-dodecyl group and R_2 represents an ethyl group.

5. A light-emitting diode as claimed in Claim 1, characterized in that R_1 represents an n-dodecyl group and R_2 represents an n-butyl group.

6. A light-emitting diode as claimed in Claim 1, characterized in that R_1 represents a 4,6,6-trimethyl heptyl group and R_2 represents a methyl group.

7. A conjugated 2,5-substituted poly(p-phenylene vinylene) comprising a repeating unit of the formula



(I)

wherein R_1 represents a C_{10}-C_{12} alkyl group and R_2 represents a C_1-C_4 alkyl group.

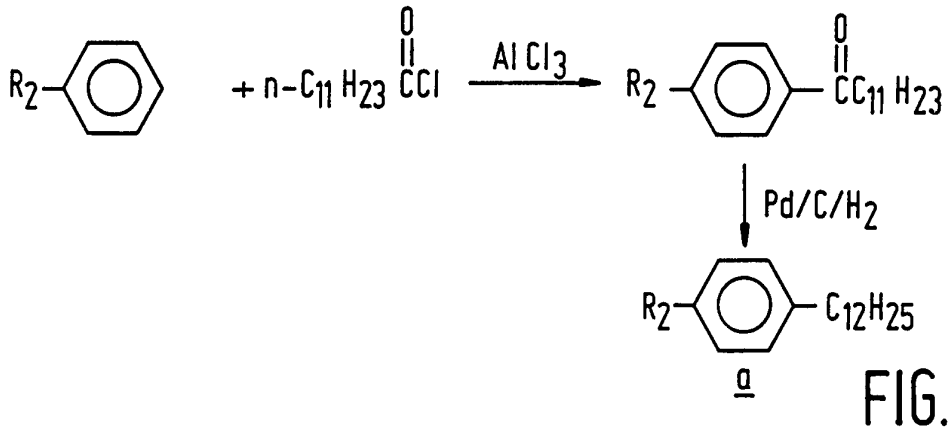
8. A conjugated 2,5-substituted poly(p-phenylene vinylene) as claimed in Claim 7, wherein R_1 is a substituent selected from the group formed by n-dodecyl, 3,7-dimethyl octyl and 4,6,6-trimethyl heptyl and R_2 represents a methyl group.

9. A method of manufacturing a light-emitting diode as claimed in Claim 1, which method comprises the following steps:

a. providing a substrate with a first, electroconductive electrode layer,

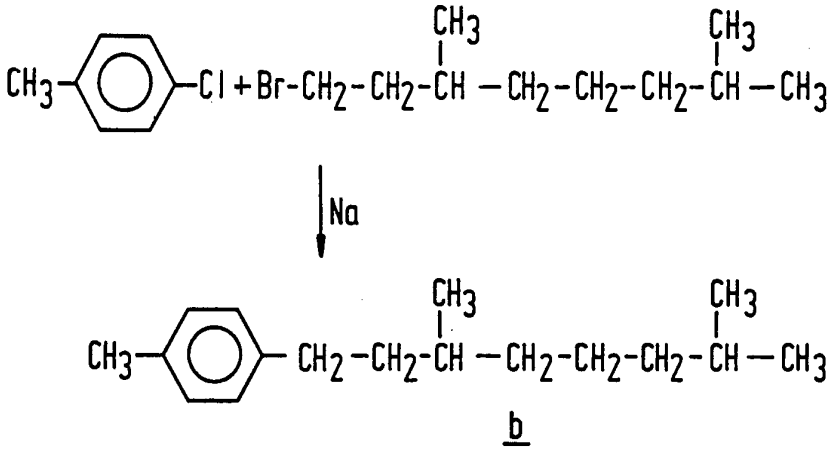
b. providing said first layer with a solution of a conjugated 2,5-substituted poly(p-phenylene vinylene) having a repeating unit in accordance with formula (I), wherein R_1 and R_2 have the above-mentioned meaning, in a solvent, whereafter the solvent is evaporated, thereby forming the active layer,

c. providing the active layer with a second, electroconductive electrode layer.



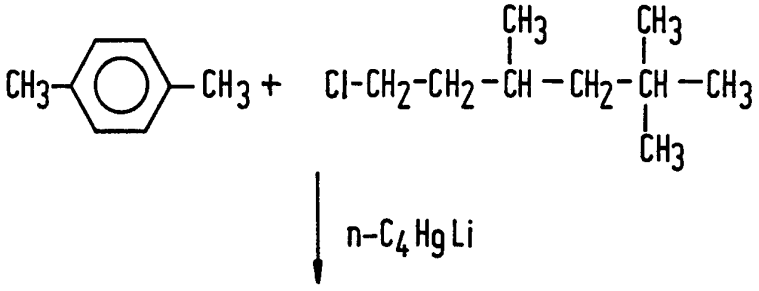
a

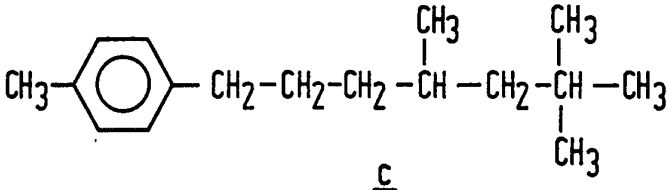
FIG.1



b

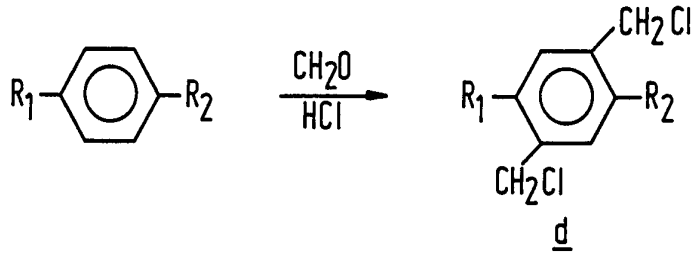
FIG.2





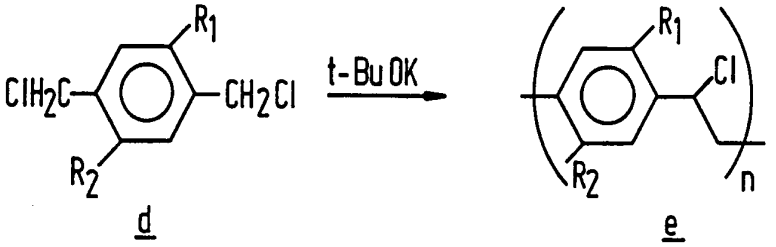
c

FIG.3

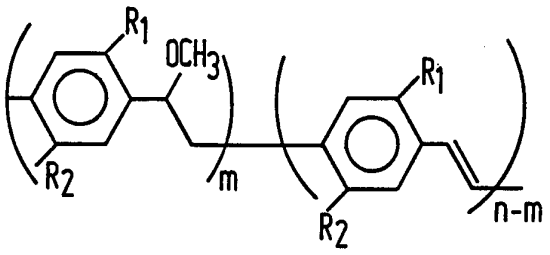


d

FIG.4

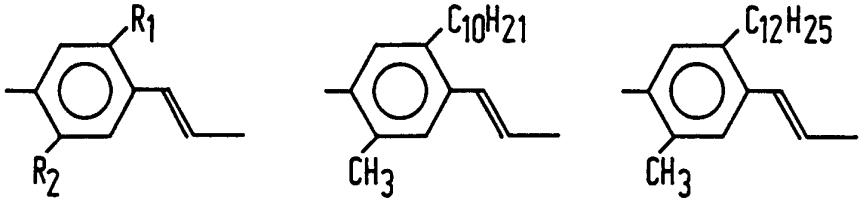


d e



f

FIG.5



(I) (II) (III)

FIG.6

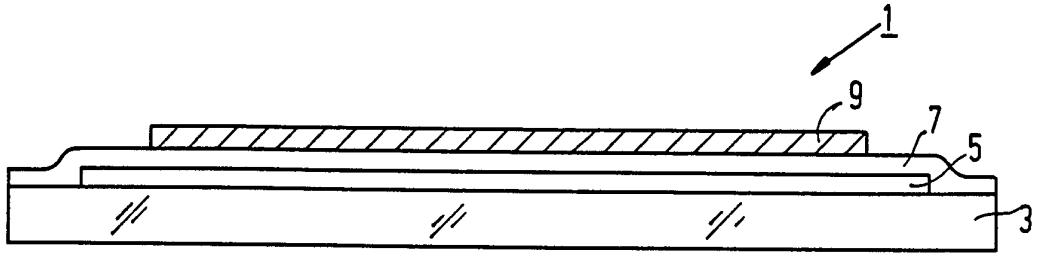


FIG.7

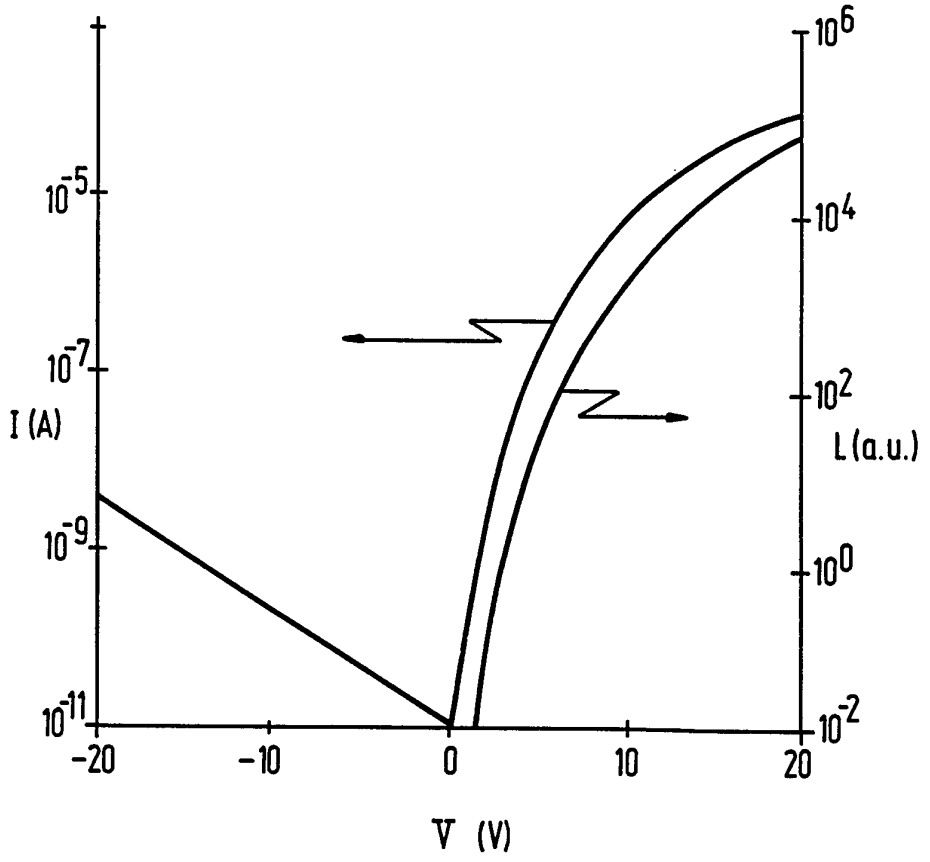


FIG.8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 95/00345

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01L 33/00, C08G 61/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08G, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, EPODOC, WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9216023 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA), 17 Sept 1992 (17.09.92) --	1-9
A	EP 0443861 A2 (SUMITOMO CHEMICAL COMPANY, LIMITED), 28 August 1991 (28.08.91) --	1-9
A	STN International, File Caplus, Caplus accession no. 1990:620894, Burroughes, J.H. et al: "Light-emitting diodes based on conjugated polymers", Nature, (London) 1990, 347(6293), 539-41 -- --------	1-12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"E" erlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 August 1995	08 -09- 1995
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Sofia Nikolopoulou Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

31/07/95

International application No.
PCT/IB 95/00345

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9216023	17/09/92	AU-A- 1445292	06/10/92
		EP-A,A- 0573549	15/12/93
		JP-T- 6508477	22/09/94
		US-A- 5408109	18/04/95
EP-A2- 0443861	28/08/91	JP-A- 3244630	31/10/91
		US-A- 5317169	31/05/94
		JP-A- 3273087	04/12/91
		JP-A- 4145192	19/05/92